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CERAMIC HEAT-INSULATION MATERIALS BASED ON SERPENTINITE

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The composition of a heat-insulating porous material based on serpentinite was developed. The naturally occurring components in the batch, including serpentinite and lacustrine diatomite, make it possible to obtain material with forsterite, whose synthesis starts at 600°C, content above 70% and to secure high porosity compared with the well-known composition. The high mechanical strength and low thermal conductivity make it possible to use the heat-insulation material for heating units and freezers.

Key words: heat-insulation material, serpentinite, diatomite, sintering, ceramic, thermal conductivity, mechanical strength, crystalline phase.

Ceramic heat-insulation materials are manufactured using mainly natural raw material (silicate rocks, slags, minerals – wollastonite, asbestos and others), obtained during mining or processing of minerals and requiring disposal in order to decrease environmental damage. Owing to the composition and structural particulars of natural raw material, ceramic heat-insulation materials possess definite characteristics such as porous structure and, in consequence, low density, low thermal conductivity and high strength, all of which promote their wide use in industrial and civil construction for heating buildings and heat insulation for hot surfaces of equipment (furnaces, boilers and pipelines) and to intensify high-temperature processes and conserve fuel. Modern inorganic heat-insulation materials are obtained on the basis of wastes from processing black shales during extraction of fine-ore mineralization [1], dust from calcination of vermiculite concentrate [2] and wastes from the enrichment of copper-nickel ores, including serpentinite minerals [3], diatomites and other forms of mineral raw materials. The use of the new ceramic heat-insulation materials based on environmentally clean, accessible mineral raw materials holds promise.

The aim of the present work is to develop a ceramic heat-insulation material using serpentinite, an environmentally clean, accessible mineral raw material formed during complex development of deposits of chromium ores and

platinum mineralization, specifically, the Aganozerskoe deposit in the Republic of Karelia.

Serpentine minerals belong to a group of hydrous magnesium silicate with the chemical formula $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. According to its crystalline structure serpentine is a complex mineral. The main minerals in the group — chrysotile, lizardite and antigorite — exhibit structural differences which in a number of cases determine the practical applications. The oxide content of serpentine is as follows: MgO — 43.0%,² SiO_2 — 44.1% and H_2O — 12.9%. The ratio between the components fluctuates in a very small range. The iron oxides FeO and Fe_2O_3 as well as NiO are present as impurities. The color of serpentine varies from dark green to greenish-black, the hardness lies in the range 2.4–3.0 and the density in the range 2.5–2.7 g/cm³ and the strength in compression is of the order of 400–625 kg/cm³. Serpentine can retain 10–13% chemically bound water at high temperatures (to about 500°C) [4].

The rocks with hydrotalcite-serpentine composition (kemistits) which we studied are, together with massive serpentinites, host rocks for chromium ores in the Aganozerskoe deposit. In integrated mining, together with serpentinites they comprise tailings, which contaminate the environment. Kemistits comprise a pelite-grussy body formed during the final stage of serpentinitization of ultramafic rock. The granulometric composition of the rocks is represented by aleurites from 0.01 to 0.1 mm as well as detrital grains of sandy, grussy and gravelly varieties of low hardness and ele-

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² Here and below the content by weight, wt.%.

TABLE 1. Chemical Compositions of the Rocks

Sample	Content, wt.-%													
	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	NiO	Cr ₂ O ₃	CO ₂	Calcination losses
Serpentine	34.06	0.21	0.51	10.02	2.03	0.12	35.69	0.50	0.03	0.02	0.38	0.30	0.57	17.00
Kemistit	32.59	0.02	0.10	9.80	3.78	0.14	37.19	0.24	0.03	0.02	0.42	0.38	0.66	15.03
Diatomite	70.46	—	1.96	2.10	—	—	0.62	0.43	0.19	0.14	—	—	—	23.33

vated acid solubility [5]. In the main the chemical composition of kemistits is no different from that of the massive serpentinites (Table 1). Kemistits possess high content of geochemically mobile forms of MgO, which makes them close to magnesite (36–42 and 45–50%, respectively), and they are valuable raw materials for obtaining high-purity MgO for metallurgy as well as nickel sulfate. Kemistits from the Aganozerskoe deposit contain the following: serpentine — 78–93%, hydrotalcite — to 10.5%, pyroaurite — to 1%, chlorite — to 3%, talc — to 2%, calcite, breunnerite and siderite — to 1.5%, biotite — to 0.3%, magnetite — to 2.5%, chromite — to 0.5%, sulfides — to 0.2%, and hydrohematite — to 0.4%. Together with a high content of MgO kemistits contain high quantities of chemical bound water (calcination losses — 15–18.5%) and very small amounts of the impurities Al₂O₃ (0.1–0.51%) and CaO (0.24–0.5%). A kemistit sample, whose chemical composition is shown in Table 1, was chosen for investigation.

The mineral composition of the samples was determined at IG KarNTs RAN by means of optical microscopy and x-ray phase analysis; the rock-forming minerals were also studied using the Vega II LSH scanning electron microscope with an INCA Energy 350 energy-dispersive analyzer. X-ray phase analysis was performed with an ARL X'TRA diffractometer with CuK₁ radiation in the angle range $2\theta = 2 - 90^\circ$, using the Siroquant software for quantitative analysis of the content of the main minerals in the sample.

X-ray phase analysis showed the kemistit sample to consist mainly of serpentine (87.8%) and hydrotalcite (12.2%) with chlorite, magnetite, chromite and iron and nickel sulfides (pyrite, marcasite, pentlandite, heazlewoodite and

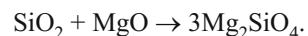
others) also being present. Microanalysis also showed that chlorite and magnetite are present in addition to serpentine (Fig. 1). The magnetite grains range in size from 0.01 to 0.2 mm, and are arranged between and inside aggregates of serpentine, often in the form of microinclusions.

According to differential-thermal analysis the serpentine in kemistit belongs to lizardite, which is characterized by strong exo (808.7–810.6°C) and endo (609–611°C) effects. Forsterite forms near 600°C [5].

Previous studies have shown that as the calcination temperature increases to 900–1000°C the density of the serpentinite samples decreases while the porosity and water absorption increase, and as process temperature increases to 1200°C an inverse dependence of these indices is observed [6]. In addition, up to 1000°C the content of the amorphous phase increases (the degree of crystallinity decreases), and as the process temperature of the serpentinites increases further the degree of crystallinity increases as a result of recrystallization.

Temperatures near 1000°C are optimal for sintering serpentinite samples, and the fine fractions in them can be used to fabricate highly effective porous articles by pressing followed by annealing.

X-ray phase analysis shows that after annealing at 980°C kemistit consists mainly of forsterite (94.8%) and periclase (5.2%) (Fig. 2). Forsterite is formed on account of serpentine according to the reactions



SiO₂ in the form of amorphous silica is present in the product of decomposition of serpentine; interacting with MgO it forms additional forsterite [4].

A kemistit sample was used as fill for the heat-insulation ceramic mix (see Table 1). Lacustrine diatomite, which is an amorphous silica sedimentary rock, was used as the curing agent. In the natural state (moisture content 80–85%) it comprises a jelly-like mass (gel) consisting of siliceous (opalin) valves of microscopic water plants (diatoms). Amorphous lacustrine diatoms of Karelia are characterized by high specific surface area 20.0–110.0 m²/g and high dispersity (granules to 110 µm). Liquid glass was used as the binding component for forming articles. The introduction of liquid glass promotes the formation of a plastic body from non-plastic disperse components.

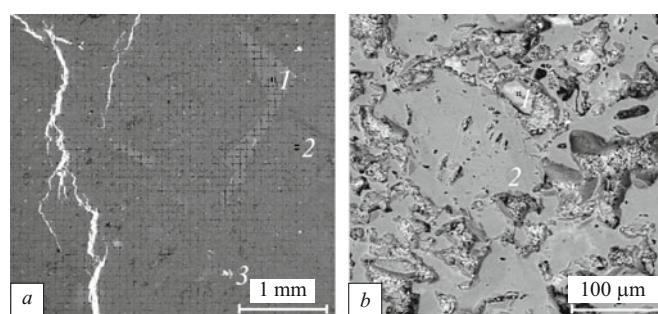


Fig. 1. Microstructures of kemistit [a: 1) chlorite; 2) serpentine; 3) magnetite] and heat-insulation material [b: 1 and 2) forsterite].

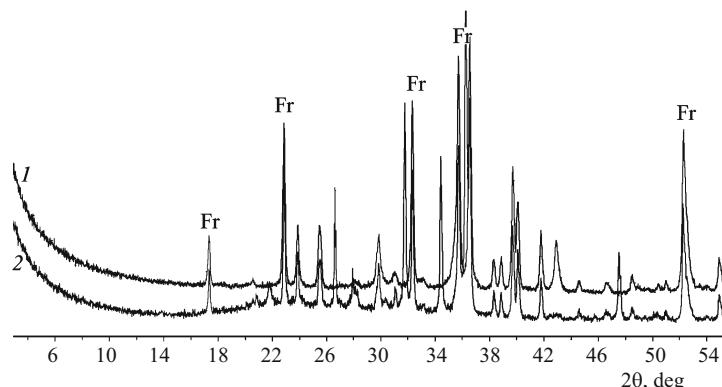


Fig. 2. X-ray diffraction patterns of kemistit (1) annealed at 980°C and heat-insulation material (2); Fr forsterite.

A ceramic body was prepared by the conventional ceramic technology. Finely comminuted components in the requisite quantities were mixed, after which sodium or potassium liquid glass with modulus 2.4 – 3.0 and density 1.36 – 1.50 g/cm³ was added to the body (Table 2). Samples with different shapes in the form of bricks and tiles were formed from the body in a laboratory press under pressure 8 – 9 MPa. The samples were annealed in a KO-14 laboratory furnace, raising the temperature to 400°C at the rate 120 K/min, and soaked for 120 min at this temperature, after which the temperature was raised to 980°C at which the samples were soaked for 2 h.

The properties of the samples formed from the ceramic body by pressing were determined in accordance with the standard procedures. The volume mass was determined according to GOST 7025–71, the moisture resistance (the capability of the material to withstand moisture without significant degradation of strength in compression) according to the strength index in compression after alternate saturations with moisture and drying, the strength in compression according to GOST 8462–85, and the thermal conductivity according to GOST 530–95. The compositions and properties of the heat-insulation material are presented in Table 2.

The investigations of the properties of the heat-insulation materials described in Table 2 showed that when a larger amount of the binding component is introduced into the ce-

ramic body No. 3 the strength of the articles increases, probably as a result of a chemical interaction of the sodium silicate glass with the mineral fill. In addition, it can be supposed that decomposition and recrystallization of the serpentine lattice, accompanied by the formation of crystalline phases in combination with the high chemical activity of lacustrine diatomite, which is finely disperse and has a high specific surface area, increase the strength of the ceramic material. Electron microscopy showed that the main crystalline phase of heat-insulation ceramic (see Fig. 1b) is forsterite, which is a product of recrystallization of serpentine. X-ray phase analysis has shown that quartz (5%), cristobalite (4%) and enstatite (7%) are present in addition to forsterite (71%) (see Fig. 2a). The amount of the glass phase is 13%. A porous structure of the material forms during annealing as a result of dehydration of chemically bound water, present in kemistit, and swelling of liquid glass as well as carbonates and hydrocarbonates, which decompose with CO₂ being released. The volume mass of the articles obtained is small, equaling 110 – 147 kg/m³. The natural components used in the batch, including serpentine, make it possible to obtain a material with forsterite content above 70%, whose synthesis starts at 600°C, and to secure high strength compared with the known composition P (see Table 2).

The heat-insulation material fabricated on the basis of serpentinite exhibits low thermal conductivity, high strength

TABLE 2. Compositions and Properties of Heat-Insulation Materials

Composition	Content, wt.%			Strength in compression, MPa	Thermal conductivity, W/(m · K)	Moisture resistance, %
	binder	curing agent	fill			
	Liquid glass	Lacustrine diatomite	Kemistit			
1	25	5	70	19.94	0.032	0.086
2	20	15	65	20.87	0.028	0.090
3	30	10	60	24.66	0.025	0.091
P*	89	5	6	1.60	0.070	2.900

* In the composition P (prototype) micaceous hydrosol (5%) was used as the curing agent (content, wt.%) and dust was used as the filler, forming during annealing of vermiculite concentration (6%). In addition, sodium alkyl silicanate was introduced in the amount 2% above 100%.

and good moisture resistance. Compared with the prototype (see Table 2) its mechanical strength is 8.0 – 15.4 times higher and the moisture resistance 32.2 – 33.7 times higher while the thermal conductivity is 2.19 – 2.8 times lower. These ensure that the new material possesses high operating performance and technological indicators. The heat-insulation material does not contain any toxic components. The economic efficiency and practicability for the manufacture of heat-insulation materials are due to the small number of components, the use of accessible naturally occurring raw materials and the simplification of the technology for obtaining porous heat-insulation materials while securing environmental safety. The high mechanical strength and low thermal conductivity make it possible to use the heat-insulation material for heating units and freezers.

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